

METHODS AND STRUCTURES FOR PRODUCTION OF
SELECTIVELY ELECTROPLATED ARTICLES

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Cross-Reference To Related Applications

(0001) This application is a Continuation-in-Part of U.S. Patent Application No. 10/144,901 filed May 13, 2002, entitled Methods and Structures for Production of Selectively Electroplated Articles, which is a Continuation-in-Part of U.S. Patent Application No. 09/498,102 filed Feb. 4, 2000, entitled Substrate Structures for Integrated Series Connected Photovoltaic Arrays and Process of Manufacture of Such Arrays, and now U.S. Patent 6,459,032 B1, which is a Continuation-in-Part of U.S. Patent Application No. 08/967,962 filed on Nov 12, 1997, entitled Substrate Structures for Integrated Series Connected Photovoltaic Arrays and Process of Manufacture of Such Arrays, and now abandoned, which is a Continuation-in-Part of U.S. Patent Application No. 08/683,061, filed July 16, 1996, entitled Substrate Structures for Integrated Series Connected Photovoltaic Arrays and Process of Manufacture of Such Arrays, and now U.S. Pat. No. 5,735,966, which is a Continuation-in-Part of U.S. Patent Application No. 08/441,552, filed May 15, 1995, entitled Substrate Structures for Integrated Series Connected Photovoltaic Arrays and Process of Manufacture of Such Arrays and now U.S. Pat. No. 5,547,516. The entire contents of the above identified applications are incorporated herein by this reference.

BACKGROUND OF THE INVENTION

(0002) Photovoltaic cells have developed according to two distinct methods. The initial operational cells employed a matrix of single crystal silicon appropriately doped to produce a planar p-n junction. An intrinsic electric field established at the p-n junction produces a voltage by directing solar photon produced holes and free electrons in opposite directions. Despite good conversion efficiencies and long-term reliability, widespread energy collection using single-crystal silicon cells is thwarted by the exceptionally high cost of single crystal silicon material and interconnection processing.

(0003) A second approach to produce photovoltaic cells is by depositing thin photovoltaic semiconductor films on a supporting substrate. These thin semiconductor films are normally less than 30 micrometers thick and typically .05 to 5 micrometers thick. Material requirements are minimized and technologies can be proposed for mass production. The thin film structures can be designed according to doped homojunction technology such as that involving silicon films, or can employ heterojunction approaches such as those using CdTe or chalcopyrite materials.

(0004) Despite significant improvements in individual cell conversion efficiencies for both single crystal and thin film approaches, photovoltaic energy collection has been generally restricted to applications having low power requirements. One factor impeding development of bulk power systems is the problem of economically collecting the energy from an extensive collection surface. Photovoltaic cells can be described as high current, low voltage devices. Typically individual cell voltage is less than one volt. The current component is a substantial characteristic of the power generated. Efficient energy

collection from an expansive surface must minimize resistive losses associated with the high current characteristic. A way to minimize resistive losses is to reduce the size of individual cells and connect them in series. Thus, voltage is stepped through each cell while current and associated resistive losses are minimized.

(0005) It is readily recognized that making effective, durable series connections among multiple small cells can be laborious, difficult and expensive. In order to approach economical mass production of series connected arrays of individual cells, a number of factors must be considered in addition to the type of photovoltaic materials chosen. These include the substrate employed and the process envisioned. Since thin films can be deposited over expansive areas, thin film technologies offer additional opportunities for mass production of interconnected arrays compared to inherently small, discrete single crystal silicon cells. Thus a number of U.S. Patents have issued proposing designs and processes to achieve series interconnections among the thin film photovoltaic cells. Many of these technologies comprise deposition of photovoltaic thin films on glass substrates followed by scribing to form smaller area individual cells. Multiple steps then follow to electrically connect the individual cells in series array. Examples of these proposed processes are presented in U.S. patents 4,443,651, 4,724,011, and 4,769,086 to Swartz, Turner et al and Tanner et al. respectively. While expanding the opportunities for mass production of interconnected cell arrays compared with single crystal silicon approaches, glass substrates must inherently be processed on an individual batch basis.

(0006) More recently, developers have explored depositing wide area films using continuous roll-to-roll processing. This technology generally involves depositing thin

films of photovoltaic material onto a continuously moving web. However, a challenge still remains regarding subdividing the expansive films into individual cells followed by interconnecting into a series connected array. For example, U.S. Patents 4,965,655 to Grimmer et. al. and U.S. Patent 4,697,041 to Okamiwa teach processes requiring expensive laser scribing and interconnections achieved with laser heat staking. In addition, these two references teach a substrate of thin vacuum deposited metal on films of relatively expensive polymers. The electrical resistance of thin vacuum metallized layers significantly limits the active area of the individual interconnected cells.

(0007) It has become well known in the art that the efficiencies of certain promising thin film photovoltaic junctions can be substantially increased by high temperature treatments. These treatments involve temperatures at which even the most heat resistant plastics suffer rapid deterioration, thereby requiring either ceramic, glass, or metal substrates to support the thin film junctions. Use of glass or ceramic substrates generally restricts one to batch processing and handling difficulty. Use of a metal foil as a substrate allows continuous roll-to-roll processing. However, despite the fact that use of a metal foil allows high temperature processing in roll-to-roll fashion, the subsequent interconnection of individual cells effectively in an interconnected array has proven difficult, in part because the metal foil substrate is electrically conducting.

(0008) U.S. Patent 4,747,618 to Nath et al. teaches a design and process to achieve interconnected arrays using roll-to-roll processing of a metal web substrate such as stainless steel. The process includes multiple operations of cutting, selective deposition, and riveting. These operations add considerably to the final interconnected array cost.

(0009) U.S. Patent 5,385,848 to Grimmer teaches roll-to-roll methods to achieve integrated series connections of adjacent thin film photovoltaic cells supported on an electrically conductive metal substrate. The process includes mechanical or chemical etch removal of a portion of the photovoltaic semiconductor and transparent top electrode to expose a portion of the electrically conductive metal substrate. The exposed metal serves as a contact area for interconnecting adjacent cells. These material removal techniques are troublesome for a number of reasons. First, many of the chemical elements involved in the best photovoltaic semiconductors are expensive and environmentally unfriendly. This removal subsequent to controlled deposition involves containment, dust and dirt collection and disposal, and possible cell contamination. This is not only wasteful but considerably adds to expense. Secondly, the removal processes are difficult to control dimensionally. Thus a significant amount of the valuable photovoltaic semiconductor is lost to the removal process. Ultimate module efficiencies are further compromised in that the spacing between adjacent cells grows, thereby reducing the effective active collector area for a given module area.

(0010) In the U.S. Patents and Applications cited above under “Cross Reference To Related Applications” Luch teaches structures for the interconnection of photovoltaic cells which employ substrates comprising electrically conductive polymer sheets. Luch showed that if one would like to adhere metal-based electrodeposits to portions of the top and/or bottom surfaces of the electrically conductive polymer sheets it would be advantageous to employ a directly electroplateable resin (DER) at the surface of the electrically conductive polymer sheet intended to be plated. Luch also taught that the electrically conductive

polymer sheet allows for the selective electrodeposition of metal-based layers. This selective electrodeposition is particularly useful in the fabrication of low-cost photovoltaic interconnecting structures.

(0011) Polymers (also referred to as plastics or resins) in general are natural electrical insulators. However, there are numerous applications of polymers in which electrical conductivity is required. Thus, many techniques have been developed to combine electrically conductive materials such as metals with polymers. For the present invention, it is understood that polymers include any of the group of synthetic or natural organic materials that may be shaped when soft and then hardened. This includes thermoplastics and three-dimensional curing materials such as epoxies and thermosets. In addition, certain silicon based materials such as silicones can be considered as polymers or resins. Polymers also include any coating, ink, or paint fabricated using a polymer binder.

(0012) A first way to impart electrical conductivity to the surface of a plastic is through simple cladding of metal foil to a polymeric substrate. A well-established application of this approach is the starting laminate structure for manufacture of many printed circuit boards.

(0013) Another way to achieve surface conductivity for a plastic article is by physically or chemically depositing metal onto a plastic substrate. Physical deposition can be achieved by arc spraying or vacuum deposition. In arc spray, a metal source is heated in an electrical arc and the heated material, at least semi-molten, is sprayed against a plastic surface. The process is generally material limited and sensitive to adhesion and part warpage issues. In vacuum deposition, a metallic source is heated or electronically

bombarded to release material in a high vacuum. This released material coats the surface of a plastic article also present in the vacuum chamber. This process is limited by high equipment cost, the necessity for vacuum processing, and material limitations. Surface conductivity can also be achieved thru the conventional physical application of conductive coatings such as electrostatic spraying of metal filled paints.

(0014) Chemical deposition of metals onto plastic substrates (for example, electroless plating) is conventionally achieved by a multi-step process. The plastic substrate is normally first chemically etched to microscopically roughen the surface. This etching promotes adhesion between the plastic substrate and the subsequently deposited metal. Further steps catalyze the plastic surface in preparation for metal deposition by chemical reduction of metal from solution. Nickel and copper are typical metals employed for “electroless plating”. “Electroless plating” comprises many steps involving expensive and harsh chemicals. This increases costs dramatically and involves environmental difficulties. The process is also very sensitive to processing variables used to fabricate the plastic substrate, limiting the applications to carefully fabricated parts and designs.

(0015) Typical thicknesses achieved with vacuum metallizing or “electroless plating” are often relatively thin. Deposition speed, equipment utilization, deposit integrity and chemical cost often restrict deposits to these relatively small thicknesses. In many cases it is desired to have increased thickness of the metal deposit. In these cases, electrodeposition is often employed following deposition of the initial conductive metal. Electrodeposited films can be quickly deposited to much greater thicknesses and variety than appropriate for vacuum metallizing or “electroless plating” techniques. In most

cases, electrodeposition is practiced in conjunction with “electroless plating” since the materials and process flow associated with vacuum metallizing the initial metal layer is somewhat incompatible with subsequent electroplating.

(0016) The type of metal chosen for electroplating, as well as the thickness of the electrodeposit will depend on the desired end use of the article. Electroplating on plastics has achieved widespread application in the area of decorative plating of plastic substrates. The plastic substrate permits the design freedom of plastics processing and a considerably lighter weight part compared to metal. Electroplating allows the aesthetic, visual aspects of metal to be incorporated into the part. Examples of these visual affects can include brightness (i.e. a highly polished surface appearance) or satin (i.e. pewter) surfaces. Typical decorative electrodeposits are relatively thick (normally a .001 inch or more of metal) and normally consist of a number of distinct layers of metal each of which is intended to perform a specific purpose such as brightness, corrosion protection etc. Examples of decorative electroplating include chrome plating of automotive articles such as grilles, or electroplating of plumbing fixtures. Decorative electroplating of plastics has been widely used since the 1970's.

(0017) In addition to imparting a decorative appearance, electroplating can also be used to impart functionality to a plastic article. In this case the metal is designed to perform a function such as carry an electrical current, or suppress electromagnetic radiation etc. In many, if not most cases, a plastic part which is electroplated to achieve functionality is not intended to be even seen by the casual consumer. Also, the nominal thickness of a functional electrodeposit will typically be less than that used for decorative applications.

(0018) In recent years a number of applications have emerged which would benefit from the characteristics offered by electrodeposition. These include flexible circuits, Molded Interconnect Devices (MID's) and EMI shielding. However, to date electrodeposition on plastic substrates to impart functionality has achieved limited use due to high costs, limited design flexibility, and process difficulties in achieving selective electrodeposition when employing conventional practices.

(0019) For purposes of the present invention, decorative electroplating is defined as a process whose primary intent is to enhance aesthetic appeal or perception of value. Functional electroplating is defined as a process whose primary intent is to achieve a performance characteristic other than aesthetic appeal such as conductivity, EMI shielding etc.

(0020) The conventional technology for electroplating on plastic (etching, chemical reduction, electroplating) has been extensively documented and discussed in the public and commercial literature. See, for example, Saubestre, Transactions of the Institute of Metal Finishing, 1969, Vol. 47., or Arcilesi et al., Products Finishing, March 1984.

(0021) Another approach to render electrical conductivity to a polymer is to synthesize an inherently conductive polymer.

(0022) Yet another approach to render electrical conductivity to a plastic is to incorporate electrically conductive fillers into the polymer itself to produce an electrically conductive polymer. The polymer acts as a matrix or binder for the conductive filler. A number of different conductive fillers can be proposed to effectively render electrical conductivity to polymers. These fillers can be finely divided, have a high aspect ratio and be metal

containing. Typical fillers are metal or metal coated powders and flake, metal or metal coated fibers such as stainless steel and nickel coated graphite, graphite itself, certain carbon blacks and inherently conductive polymers.

(0023) In a discussion of polymers rendered electrically conductive by loading with electrically conductive fillers, it may be important to distinguish between “microscopic resistivity” and “bulk” or “macroscopic resistivity”. “Microscopic resistivity” refers to a characteristic of a polymer/filler mix considered at a relatively small linear dimension of for example 1 micrometer or less. “Bulk”, or “macroscopic resistivity” refers to a characteristic determined over larger linear dimensions. To illustrate the difference between “microscopic” and “bulk, macroscopic” resistivities, one can consider a polymer loaded with conductive fibers at a fiber loading of 10 weight percent. Such a material might show a low “bulk, macroscopic” resistivity when the measurement is made over a relatively large distance. However, because of fiber separation (holes) such a composite might not exhibit consistent “microscopic” resistivity.

(0024) Electrically conductive polymers, plastics, and resins produced by loading with electrically conductive fillers have found applications in areas such as electromagnetic interference (EMI) shielding and self regulating electrical heating resistors. However, in many applications their sole use is prohibited by a number of factors. Problems can occur in achieving mechanical joining and electrical communication between the electrically conductive resin and other parts of an electrical device. A limited selection of material choices is available and the compounded materials are relatively expensive. Furthermore, many of the electrically conductive fillers are abrasive to processing equipment and alter

fabrication characteristics adversely. Also, their intrinsic resistivity is somewhat higher than that available from solid metals and in certain instances a thin "skin" of non-conductive polymer can form on the surface.

(0025) In addition to simply imparting conductivity to a plastic, there are many applications where it is advantageous to selectively combine an electrically conducting material such as a metal with an electrically insulating material such as a plastic. In most cases selectively conductive articles include insulating surfaces being positioned contiguous or adjacent to conductive surfaces. Typical applications for such selective material placement include electrical circuit patterns, antennas, solar energy collectors etc. Many of these applications are difficult using currently available techniques. With regard to non-conductive plastic substrates, the art has developed a variety of manufacturing processes which fall into the broad categories of "subtractive" or "additive" techniques.

(0026) With subtractive processes, a layer of metal is first deposited over the entire surface of a plastic substrate by cladding, spraying, vacuum or chemical deposition. This is followed by removal of portions of the metal layer, leaving the desired selective metal pattern. This is a practice widely used to manufacture printed circuits, wherein the desired metal removal is accomplished by photoetch techniques. These metal removal techniques are expensive, design limited, wasteful of material and environmentally difficult due the necessity of required disposal of spent etching solution.

(0027) Additive processes, on the other hand, deposit metal on selective portions of the plastic substrate. In the case of the physical deposition techniques described above such as arc spraying, conventional spraying, and vacuum metallizing, metal will coat every

surface in a line of sight to the source. Masking those areas intended to be protected from metal deposition can be suggested, but masking can be difficult, expensive and is impractical with complex designs such as three-dimensional articles.

(0028) A number of techniques have been employed to selectively metallize plastic substrates using “electroless” chemical deposition or “electroless plating”. The “electroless” process is designed to coat the entire substrate surface with a metal. It is important to note that immersion processes such as electroless plating or electroplating differ from other metallization processes in that normally the entire object is exposed to the process (or source of metal). When attempts are made to achieve selective plating, the fact that the surface areas intended to remain unplated are exposed to the plating solution often results in undesirable problems. Thus many attempts to achieve selective electroplating have involved preventing selective portions of the surface from being exposed to the process i.e. by masking etc.

(0029) One approach to achieve selective conductivity has been to employ two material (also known as two-shot, dual shot, multi-shot etc.) moldings with only one of the materials being specially formulated to be “receptive” to electroless chemical deposition of a metal. This is accomplished by incorporating a plating catalyst directly into a resin and then combining this “catalyzed” resin portion with an “uncatalyzed” resin portion. Conceptually, only those surfaces of the article formed by the “catalyzed” resin will stimulate the reaction reducing metal, and thus only those surfaces will be metallized. Examples of these techniques are found in U.S. Patent 6,137,452 to Sullivan and European Patent Application EP1069209. This approach is slow, expensive and can be

difficult and unpredictable especially on complex parts. Poor line definition, “skip plating” and complete part coverage due to bath instabilities often occur. Despite much effort to develop consistent and reliable performance through material and process development, these techniques remain expensive, difficult, and unpredictable.

(0030) Another approach to achieve selective “electroless” metallization of plastics has been to selectively apply plating stopoff lacquers, or plating resists to the surface of the plastic substrates. These stop-offs prevent chemical plating on the areas to which they are applied. See for example U.S. Patent 4,224,118 to Hans. These processes are expensive, environmentally difficult, and often impractical when considering complex three-dimensional substrates.

(0031) Yet another approach to achieve selective “electroless” plating has been to selectively deposit a “seed” layer of metal plating catalyst such as palladium by using phototechniques. Subsequent “electroless” plating will only deposit metal in areas populated by this “seed” layer. See for example U.S. Patent 6,210,781 to Baum et. al., and U.S. Patent 5,468,597 to Calabrese et. al. As with the stopoffs and plating resists described above, these processes are expensive, environmentally difficult, and often impractical when considering complex three-dimensional substrates.

(0032) In applications requiring selective placement of electrically conductive material, one can consider electrodeposition onto a selectively positioned electrically conductive polymer to augment the electrical conductivity supplied by the resin. It is understood that such selective positioning of the electrically conductive polymeric material can be achieved by any number of known processing techniques such as application of an electrically

conductive polymeric based coating or ink or fabrication of an electrically conductive thermoplastic polymer or fabrication of an electrically conductive three-dimensional curing polymer. A coating or ink can be considered as a substance spread over a surface and can be applied with the assistance of a water or solvent based carrier. Alternatively, phase change coatings can be considered for the coating applications of the present invention.

(0033) When considering producing an electrically conductive polymer intended to be electroplated, one should consider “microscopic” resistivity in order to achieve uniform, “hole-free” deposit coverage. Thus, the fillers chosen will likely comprise those that are relatively small, but with loadings sufficient to supply the required conductive contacting. Such fillers include metal powders and flake, metal coated mica or spheres, conductive carbon black and the like.

(0034) Efforts to advance systems contemplating metal electrodeposition directly onto the surface of an electrically conductive polymer have encountered a number of obstacles. The first is the combination of fabrication difficulty and material property deterioration brought about by the heavy filler loadings often required. A second is the high cost of many conductive fillers employed such as silver flake.

(0035) Another major obstacle involved in the electroplating of electrically conductive polymers is a consideration of adhesion between the electrodeposited metal and polymeric substrate (metal/polymer adhesion). In some cases such as electroforming, where the electrodeposited metal is eventually removed from the substrate, metal/polymer adhesion may actually be detrimental. However, in most cases sufficient adhesion is required to prevent metal/polymer separation during extended environmental and use cycles.

(0036) A number of methods to enhance adhesion have been employed. For example, etching of the surface prior to plating can be considered. Etching can be achieved by immersion in vigorous solutions such as chromic/sulfuric acid. Alternatively, or in addition, an etchable species can be incorporated into the conductive polymeric compound. The etchable species at exposed surfaces is removed by immersion in an etchant prior to electroplating. Oxidizing surface treatments can also be considered to improve metal/plastic adhesion. These include processes such as flame or plasma treatments or immersion in oxidizing acids.

(0037) In the case of conductive polymers containing finely divided metal, one can propose achieving direct metal-to-metal adhesion between electrodeposit and filler. However, here the metal particles are generally encapsulated by the resin binder, often resulting in a resin rich “skin”. To overcome this effect, one could propose methods to remove the “skin”, exposing active metal filler to bond to subsequently electrodeposited metal.

(0038) Another approach to impart adhesion between conductive resin substrates and electrodeposits is incorporation of an “adhesion promoter” at the surface of the electrically conductive resin substrate. This approach was taught by Chien et al. in U.S. Patent No. 4,278,510 where maleic anhydride modified propylene polymers were taught as an adhesion promoter. Luch, in U.S. Patent No. 3,865,699 taught that certain sulfur bearing chemicals could function to improve adhesion of initially electrodeposited Group VIII metals.

(0039) An additional major obstacle confronting development of electrically conductive polymeric resin compositions capable of being directly electroplated is the initial “bridge” of electrodeposit on the surface of the electrically conductive resin. In electrodeposition, the substrate to be plated is normally made cathodic through a pressure contact to a metal rack tip, itself under cathodic potential. However, if the contact resistance is excessive or the substrate is insufficiently conductive, the electrodeposit current favors the rack tip to the point where the electrodeposit will not bridge to the substrate.

(0040) Moreover, a further problem is encountered even if specialized racking successfully achieves electrodeposit bridging to the substrate. Many of the electrically conductive polymeric resins have resistivities far higher than those of typical metal substrates. The polymeric substrate can be relatively limited in the amount of electrodeposition current which it alone can convey. Thus, the conductive polymeric substrate does not cover almost instantly with electrodeposit as is typical with metallic substrates. Except for the most heavily loaded and highly conductive polymer substrates, a large portion of the electrodeposition current must pass back through the previously electrodeposited metal growing laterally over the surface of the conductive plastic substrate. In a fashion similar to the bridging problem discussed above, the electrodeposition current favors the electrodeposited metal and the lateral growth can be extremely slow and erratic. This restricts the size and “growth length” of the substrate conductive pattern, increases plating costs, and can also result in large non-uniformities in electrodeposit integrity and thickness over the pattern.

(0041) This lateral growth is dependent on the ability of the substrate to convey current. Thus, the thickness and resistivity of the conductive polymeric substrate can be defining factors in the ability to achieve satisfactory electrodeposit coverage rates. When dealing with selectively electroplated patterns long thin metal traces are often desired, deposited on a relatively thin electrically conductive polymer substrate. These factors of course work against achieving the desired result.

(0042) This coverage rate problem likely can be characterized by a continuum, being dependent on many factors such as the nature of the initially electrodeposited metal, electroplating bath chemistry, the nature of the polymeric binder and the resistivity of the electrically conductive polymeric substrate. As a “rule of thumb”, the instant inventor estimates that coverage rate problems would demand attention if the resistivity of the conductive polymeric substrate rose above about .001 ohm-cm.

(0043) Beset with the problems of achieving adhesion and satisfactory electrodeposit coverage rates, investigators have attempted to produce directly electroplateable polymers by heavily loading polymers with relatively small metal containing fillers. Such heavy loadings are sufficient to reduce both microscopic and macroscopic resistivity to a level where the coverage rate phenomenon may be manageable. However, attempts to make an acceptable directly electroplateable resin using the relatively small metal containing fillers alone encounter a number of barriers. First, the fine metal containing fillers are relatively expensive. The loadings required to achieve the particle-to-particle proximity to achieve acceptable conductivity increases the cost of the polymer/filler blend dramatically. The metal containing fillers are accompanied by further problems. They tend to cause

deterioration of the mechanical properties and processing characteristics of many resins. This significantly limits options in resin selection. All polymer processing is best achieved by formulating resins with processing characteristics specifically tailored to the specific process (injection molding, extrusion, blow molding etc.). A required heavy loading of metal filler severely restricts ability to manipulate processing properties in this way. A further problem is that metal fillers can be abrasive to processing machinery and may require specialized screws, barrels, and the like. Finally, despite being electrically conductive, a simple metal-filled polymer still offers no mechanism to produce adhesion of an electrodeposit since the metal particles are generally encapsulated by the resin binder, often resulting in a non-conductive resin-rich "skin". For the above reasons, fine metal particle containing plastics have not been widely used as substrates for directly electroplateable articles. Rather, they have found applications in production of conductive adhesives, pastes, and paints.

(0044) The least expensive (and least conductive) of the readily available conductive fillers for plastics are carbon blacks. Attempts have been made to produce electrically conductive polymers based on carbon black loading intended to be subsequently electroplated. Examples of this approach are the teachings of U.S. Patents 4,038,042, 3,865,699, and 4,278,510 to Adelman, Luch, and Chien et al. respectively.

(0045) Adelman taught incorporation of conductive carbon black into a polymeric matrix to achieve electrical conductivity required for electroplating. The substrate was pre-etched in chromic/sulfuric acid to achieve adhesion of the subsequently electroplated metal. A fundamental problem remaining unresolved by the Adelman teaching is the

relatively high resistivity of carbon loaded polymers. The lowest "microscopic resistivity" generally achievable with carbon black loaded polymers is about 1 ohm-cm. This is about five to six orders of magnitude higher than typical electrodeposited metals such as copper or nickel. Thus, the electrodeposit bridging and coverage rate problems described above remained unresolved by the Adelman teachings.

(0046) Luch in U.S. Patent 3,865,699 and Chien et al. in U.S. Patent 4,278,510 also chose carbon black as an electrically conductive filler for polymeric compounds to be electroplated. However, these inventors further taught incorporation of an electrodeposit coverage or deposition rate accelerator to overcome the galvanic bridging and lateral electrodedeposit growth rate problems described above. In the embodiments, examples and teachings of U.S. Patents 3,865,699 and 4,278,510, it was shown that certain sulfur bearing materials, including elemental sulfur, can function as electrodeposit coverage or growth rate accelerators to overcome those problems associated with electrically conductive polymeric substrates having relatively high resistivity. In addition to elemental sulfur, sulfur in the form of sulfur donors such as sulfur chloride, 2-mercaptopbenzothiazole, N-cyclohexyle-2-benzothiaozole sulfonamide, dibutyl xanthogen disulfide, and tetramethyl thiuram disulfide or combinations of these and sulfur were identified. Those skilled in the art will recognize that these sulfur donors are the materials which have been used or have been proposed for use as vulcanizing agents or accelerators. Since the polymer-based compositions taught by Luch and Chien et al. could be electroplated directly they could be accurately defined as directly electroplateable resins (DER). These

resins can be generally described as electrically conductive polymers with the inclusion of a growth rate accelerator.

(0047) Specifically for the present invention, directly electroplateable resins, (DER), are characterized by the following features.

- (a) having a polymer or resin matrix or binder;
- (b) presence of conductive fillers in the polymer matrix in amounts sufficient to provide an electrical volume resistivity of the polymer/conductive filler mix, which is sufficiently low to allow direct electrodeposition. Typically, a resistivity less than 1000 ohm-cm., e.g., 100 ohm-cm., 10 ohm-cm., 1 ohm-cm. .1 ohm-cm., .01 ohm-cm., .001 ohm-cm., suffices;
- (c) presence of an electrodeposit coverage rate accelerator;
- (d) presence of the polymer, conductive filler and electrodeposit coverage rate accelerator in the directly electroplateable composition in cooperative amounts required to achieve direct coverage of the composition with an electrodeposited metal or metal-based alloy. It has been found that Group VIII metals or Group VIII metal-based alloys are particularly suitable as the initial electrodeposit on the DER surface.

(0048) It is understood the electrical conductivity required to allow for direct electrodeposition can also be achieved thru the use of an inherently conductive polymer.

In this instance it may not be necessary to add electrical fillers to the polymer.

(0049) In his Patents, Luch specifically identified unsaturated elastomers such as natural rubber, polychloroprene, butyl rubber, chlorinated butyl rubber, polybutadiene rubber,

acrylonitrile-butadiene rubber, styrene-butadiene rubber etc. as suitable for the matrix polymer of a directly electroplateable resin. Other polymers identified by Luch as useful included polyvinyls, polyolefins, polystyrenes, polyamides, polyesters and polyurethanes.

(0050) When used alone, the minimum workable level of carbon black required to achieve "microscopic" electrical resistivities of less than 1000 ohm-cm. for a polymer/carbon black mix appears to be about 8 weight percent based on the combined weight of polymer plus carbon black. The "microscopic" material resistivity generally is not reduced below about 1 ohm-cm. by using conductive carbon black alone. This is several orders of magnitude larger than typical metal resistivities. Other well known, finely divided highly conductive fillers (such as metal flake) can be considered in DER applications requiring lower "microscopic" resistivity. In these cases the more highly conductive fillers can be used to augment or even replace the conductive carbon black.

(0051) The "bulk, macroscopic" resistivity of conductive carbon black filled polymers can be further reduced by augmenting the carbon black filler with additional highly conductive, high aspect ratio fillers such as metal containing fibers. This can be an important consideration in the success of certain applications. Furthermore, one should realize that incorporation of non-conductive fillers may increase the "bulk, macroscopic" resistivity of conductive polymers loaded with finely divided conductive fillers without significantly altering the "microscopic resistivity" of the conductive polymer.

(0052) It is important to recognize a number of important characteristics of directly electroplateable resins (DERs) which facilitate the current invention. First, regarding electrodeposit coverage rate accelerators, both Luch and Chien et al. in the above

discussed U.S. Patents demonstrated that sulfur and other sulfur bearing materials such as sulfur donors and accelerators served this purpose when using an initial Group VIII “strike” layer. One might expect that other elements of Group 6A nonmetals, such as oxygen, selenium and tellurium, could function in a way similar to sulfur. In addition, other combinations of electrodeposited metals and nonmetal coverage rate accelerators may be identified. It is important to recognize that such an electrodeposit coverage accelerator is extremely important in order to achieve direct electrodeposition in a practical way onto polymeric substrates having relatively high resistivity compared to metals (i.e. .001 ohm-cm. or above) or very thin electrically conductive polymeric substrates having restricted current carrying ability.

(0053) A second important characteristic of directly electroplateable resins is that electrodeposit coverage speed depends not only on the presence of an electrodeposit coverage rate accelerator but also on the “microscopic resistivity” and less so on the “macroscopic resistivity” of the DER formulation. Thus, large additional loadings of functional non-conductive fillers can be tolerated in DER formulations without undue sacrifice in electrodeposit coverage or adhesion. These additional non-conductive loadings do not greatly affect the “microscopic resistivity” associated with the polymer/conductive filler/electrodeposit coverage accelerator “matrix” since the non-conductive filler is essentially encapsulated by ”matrix” material. Conventional “electroless” plating technology does not permit this compositional flexibility.

(0054) A third important characteristic of DER technology is its ability to employ polymer resins generally chosen in recognition of the fabrication process envisioned and the

intended end use requirements. For example, should an extrusion blow molding fabrication be desired, resins having the required high melt strength can be employed. Should the part be injection molded and have thin wall cross-sections, a typical situation encountered in selective design of conductive trace patterns, a high flow resin can be chosen. Should a coating, ink, paint, or paste be envisioned, a soluble resin such as an elastomer can be considered. All polymer fabrication processes require specific resin processing characteristics for success. The ability to “custom formulate” DER’s to comply with these changing processing and end use requirements while still allowing facile, quality electroplating is a significant factor in the selective electroplating teachings of the current invention. Conventional “electroless” plating technology does not permit great flexibility to “custom formulate”.

(0055) Due to multiple performance problems associated with their intended end use, none of the attempts identified above to directly electroplate selectively positioned electrically conductive polymers or plastics has ever achieved any recognizable commercial success. Nevertheless, the current inventor has persisted in personal efforts to overcome certain performance deficiencies associated with the initial DER technology. Along with these efforts has come a recognition of unique and eminently suitable applications employing the DER technology especially for those applications requiring selective placement of metal patterns and particularly metal-based electrodeposits. Some examples of these unique applications for selectively electroplated articles include electrical circuits, electrical traces, circuit boards, antennas, capacitors, induction heaters, connectors, switches, resistors, inductors, batteries, fuel cells, coils, signal lines, power

lines, radiation reflectors, coolers, diodes, transistors, piezoelectric elements, photovoltaic cells, emi shields, biosensors and sensors. One readily recognizes that the demand for such functional applications for selectively electroplated articles is relatively recent and has been particularly explosive during the past decade.

(0056) In order to eliminate ambiguity in terminology, for the present invention the following definitions are supplied:

(0057) "Metal-based" refers to a material or structure having at least one metallic property and comprising one or more components at least one of which is a metal or metal-containing alloy.

(0058) "Alloy" refers to a substance composed of two or more intimately mixed materials.

(0059) "Group VIII metal-based" refers to a substance containing by weight 50% to 100% metal from Group VIII of the Periodic Table of Elements.

OBJECTS OF THE INVENTION

(0060) An object of the invention is to provide new materials for selectively electroplated articles.

(0061) A further object of the invention is to provide novel methods of facile manufacture of selectively electroplated articles.

(0062) A further object of the invention is to expand permissible design options for the production of selectively electroplated articles.

SUMMARY OF THE INVENTION

(0063) The current invention involves production of selectively electroplated articles comprising directly electroplateable resins. In preferred embodiments the directly electroplateable resin is further coated with an adherent layer of highly conductive electrodeposit. Novel manufacturing methods and unique selectively electroplated structures made possible by the use of directly electroplateable resins are taught.

BRIEF DESCRIPTION OF THE DRAWINGS

(0064) The various factors and details of the structures and manufacturing methods of the present invention are hereinafter more fully set forth with reference to the accompanying drawings wherein:

(0065) Figure 1 is a view of one embodiment of the invention.

(0066) Figure 2 is a view of another embodiment of the invention.

(0067) Figure 2A is an embodiment similar to Figure 2 but incorporating a modified structure.

(0068) Figure 3 is a view of an additional embodiment illustrating an article employed in an Example of the practice of the invention.

(0069) Figure 4 is a plan view of an electrical circuit pattern made possible by the selective electroplating of a directly electroplateable resin.

(0070) Figure 5 is a sectional view taken substantially along the line 5-5 of Figure 4.

(0071) Figure 6 is a view of the article of Figure 5 following an additional processing step.

(0072) Figure 7 is a plan view of an additional three-dimensional electrical circuit pattern made possible by using a directly electroplateable resin.

(0073) Figure 8 is a sectional view taken substantially along the line 8-8 of Figure 7.

(0074) Figure 9 is a sectional view of the article of Figures 7 and 8 following an additional processing step.

(0075) Figure 10 is a top plan view of an embodiment of a novel substrate structure useful in the manufacture of series interconnected photovoltaic arrays.

(0076) Figure 11 is a sectional view similar to taken substantially along line 11-11 of Figure 10.

(0077) Figure 11A is a view similar to Figure 11 following an additional processing step.

(0078) Figure 12 is a top plan view of a substrate structure for achieving series interconnections of thin film photovoltaic cells.

(0079) Figure 13 is a sectional view taken substantially along the lines 13-13 of Fig. 12.

(0080) Figure 13A is a view of an additional embodiment of the invention.

(0081) Figure 13B is a view similar to Figure 13A following an additional processing step.

(0082) Figure 14 is a sectional view similar to Figure 13 showing an alternate embodiment of a substrate structure for achieving series interconnections of photovoltaic cells.

(0083) Figure 15 is a top plan view of a starting material for another embodiment of the invention.

(0084) Figure 16 is a greatly magnified plan view of the material of FIG. 15.

(0085) Figure 17 is a sectional view taken substantially along line 17-17 of FIG. 16.

(0086) Figure 18 is a sectional view taken substantially along line 18-18 of FIG. 16.

(0087) Figure 19 is a view similar to FIG. 15 but defining three distinct area portions of the structure produced by a process step.

(0088) Figure 20 is a greatly magnified plan view of that portion of FIG. 19 defined by "W2".

(0089) Figure 21 is a greatly magnified sectional view of a portion of the structure of FIG. 20 taken substantially from the perspective of line 21-21 of FIG. 20.

(0090) Figure 22 is a sectional view similar to FIG. 21 showing the structure following an optional additional process step.

(0091) Figure 23 is a plan view of the starting structure for another embodiment of the selective electroplating use of DER.

(0092) Figure 24 is plan view similar to FIG. 23 following an additional processing step.

(0093) Figure 25 is a sectional view taken substantially from the perspective of lines 25-25 of FIG. 24.

(0094) Figure 26 is a view similar to FIG. 25 following an additional processing step in the production of the selectively plated article.

(0095) Figure 26A is a view similar to FIG 26 following an additional optional process step.

(0096) Figure 27 is a sectional view of an alternate form of structure of the embodiment shown in FIG. 26.

(0097) Figure 28 is a top plan view of a starting article illustrating another embodiment of the present invention.

(0098) Figure 29 is a sectional view taken substantially from the perspective of lines 29-29 of Figure 28.

(0099) Figure 30 is a view similar to FIG. 29 following an additional processing step.

(0100) Figure 31 is a sectional view similar to FIG. 29 of a modified embodiment.

(0101) Figure 32 is a view similar to FIG. 31 following an additional processing step.

DESCRIPTION OF PREFERRED EMBODIMENTS

(0102) Reference will now be made in detail to the preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings. In the drawings, like reference numerals designate identical or corresponding parts throughout several views and an additional letter designation is characteristic of a particular embodiment.

(0103) While not precisely definable, for the present invention, electrically insulating materials may generally be characterized as having electrical resistivities greater than 10,000 ohm-cm. Also, for the present invention, electrically conductive materials may generally be characterized as having electrical resistivities less than 10,000 ohm-cm. Also for the present invention, electrically resistive materials may generally be characterized as having electrical resistivities in the range of .001 ohm-cm to 10,000 ohm-cm.

(0104) In the embodiments to follow, the structures can be characterized as being defined by one or more exterior or exposed surfaces or surface regions. For the present invention, an exterior or exposed surface or surface region is defined as one which is intended to

contact the electroplating solution when the structure is immersed in an electroplating bath.

(0105) The following teaching of preferred embodiments, taken along with the descriptive figures, will reveal and teach the eminently suitable characteristics of directly electroplateable resins in the production of selectively electroplated articles. In the following, the acronym "DER" will be used to designate a directly electroplateable resin. A number of unique characteristics of DER's contribute to the success of these combinations. Specifically, recent development of high flow formulations has been demonstrated permitting molding of thin-walled sections. Such small cross sectional traces are often required to achieve the selectively electroplated patterns currently demanded. High loadings of additional fillers, such as glass fiber, has been demonstrated to solve dimensional stability and shrinkage issues without affecting plateability. This is a result of the recognition that plateability issues with DER's are controlled by "microscopic resistivity" rather than "macroscopic resistivity". The ability to custom formulate DER's further allows production of complex, selectively plated structures using processing techniques such as injection molding, dual shot molding (two color molding), overmolding, blow molding, extrusion, co-extrusion, thermoforming, stamping, printing, and coating. These and other attributes of DER's in production of selectively electroplated articles will become clear through the following remaining specification, accompanying figures and claims.

(0106) Referring to FIG. 1, there is shown a view of a portion of an article, generally designated by numeral 1, intended to exhibit a "soft-touch" effect. Article 1 is an

intermediate article of manufacture comprising “islands” of thermoplastic elastomer 2 embedded in a matrix of DER 3. FIG. 1 could, for example, be a schematic representation of a handle for a tool or personal care item. Subjecting intermediate article 1 to an electroplating process results in metal-based electrodeposit coating only the exposed surface regions of DER 3, leaving the insulating thermoplastic elastomer regions 2 uncoated. The electrodeposit coating could impart desired metallic characteristics such as a bright polished finish, and yet the article retains its “soft-touch” quality.

(0107) Referring now to FIG. 2, an additional embodiment of the invention, generally designated by numeral 6, is shown. Article 6 illustrates a pressure contact intended to supply electrical communication between circuit components 7 and 8. A layer portion of elastomer 9 spans positioning components 10 and 11. Bonded to elastomer 9 is DER portion 13. Bonded to DER portion 13 is electrodeposited metal-based layer 12. In this and in other embodiments of the present invention the electrodeposit is understood to be either a single layer or multiple layers of metal-based material as is understood in the electroplating art. Alternatively elastomer 9 can serve as the matrix material for a DER composition and electrodeposit 12 could be adhered directly to elastomer 9. This structure would therefore eliminate DER material 13. One readily recognizes that application of pressure in the direction of arrow “P” will result in electrical communication between circuit elements 7 and 8, while release of that pressure will result in loss of the communication due the elastomer returning towards its original shape due to its resilient nature.

(0108) Figure 2A shows an alternate embodiment of the invention generally designated by 15. Article 15 illustrates a pressure contact similar in its operation to Article 6 of FIG. 2. Article 15 retains the positioning components 10a and 11a. However, in Article 15 a DER comprising an elastomeric matrix 14 (shown in phantom) is integrally joined to insulating elastomer portions 9a. Thus the separate DER layer 13 of FIG. 2 is replaced by DER portion 14 which is integrally bonded to insulating elastomeric portions 9a. Electrodeposit 12a covers the initially exposed surface of DER material 14. It is understood that appropriate application of an insulating stopoff would prevent electrodeposition on selected areas of DER material 14 if desired. One readily recognizes that this embodiment demonstrates the ability to selectively electroplate an elastomeric article.

(0109) FIG. 3 depicts a front face housing for a cellular phone, generally identified by numeral 16. Housing 16 consists of a thermoplastic elastomer 17 attached to a directly electroplateable resin indicated by numeral 18. As will be demonstrated in Example 1, DER portion 18 can be selectively metallized to provide a unique combination of an electroplated metal and thermoplastic elastomer.

(0110) Another functional application using the selectivity of DER is illustrated in Figures 4 and 5. Figures 4 and 5 show a DER material 21 fabricated in a loop design. This is achieved by depositing the DER material into channels on an otherwise substantially flat electrically insulating material 22. Alternatively, the DER material 21 could be deposited directly onto the surface of the electrically insulating material 22. In the embodiment, DER material 21 is positioned contiguous to or adjacent the electrically insulating material

22. Additionally mounting pads 23 and wells 24 are incorporated into the DER portion of the multi-material article. Subjecting the article illustrated in Figures 4 and 5 to an electroplating step results in the article illustrated in Figure 6. In Figure 6, electrodeposit 25 is deposited selectively on the surface of DER material 21, leaving the surface of 22 electrically insulating. It is understood that electrodeposit 25 is in direct contact with DER material 21. It is also understood that wells 24 and pads 23 will also cover with electrodeposit. The electrodedeposit coating the surface of wells 24 allows excellent ohmic contact to the connector pins of a microchip, while the electrodedeposit on the loop structure gives a robust and highly conductive antenna for transformer power transmission. These features are highly desirable in the production of “smart cards” and/or “rfid tags” used for convenient transportable information storage.

(0111) In some embodiments, material 22 positioned contiguous to DER material 21 could comprise certain electrically conductive materials. This is permissible as long as the electrically conductive material 22 is sufficiently resistive to prevent any reasonable lateral growth of electrodeposited metal over its surface. The essential requirement is that the DER material 21 is covered with a metal-based electrodedeposit while material 22 remains essentially uncovered. This is a result of the unique selectivity afforded by the coverage rate accelerators included in DER’s.

(0112) An additional application for the electrodeposition selectivity of DER materials is illustrated in Figures 7 through 9. These Figures illustrate a multicomponent article using DER to produce a conductive trace on a geometrically complex three-dimensional molding. In Figures 7 through 9, DER material is identified as numeral 31, and non-

conductive material as 32. It is contemplated that the article illustrated in Figures 7 and 8 is produced by a multi-component (generally referred to as a multi color or dual shot) molding process. Figures 7 and 8 also illustrate a well 33 and through-hole 34 which are molded into the object. Figure 9 illustrates the article following exposure to an electroplating process. In Figure 9, numeral 35 illustrates an electrodeposit. Electrodeposit 35 is understood to be either a single layer or multiple layers of metal as is understood in the electroplating art. The electrodeposit supplies a robust highly conductive circuit in a pattern difficult to achieve by alternate conventional techniques.

(0113) Figure 10 shows yet another embodiment of the current disclosure. The plan view of 10 illustrates a polymer based sheet 38 of width "W" subdivided into three areas "W1", "W2", and "W3". Polymer based sheet 38 can be conveniently formed by coextrusion of materials 39A, 39B, and 39C, corresponding to regions "W1", "W2", and "W3" respectively. Materials 39A, 39B, and 39C can be all based on the same polymer or different polymers can be chosen. It is important however that proper joining integrity be established at mating interfaces 40 and 41.

(0114) The material 39B chosen for region "W2" is an electrically conductive polymer sheet. In addition, it may be advantageous to electroplate the polymer sheet, in which case a sheet comprising DER would be a preferred choice. Holes 42 are positioned in electrically conductive sheet 39B.

(0115) Figure 11 is a sectional view taken substantially along line 11-11 of Figure 10. As shown in Figures 10 and 11, region "W2" is caused to have holes 42 along its length. In the simplest conceptual case, these holes are simply punched in the region "W2". Another

approach would be to formulate the region “W2” of Figures 10 and 11 from a fabric (non-woven or woven) of electrically conductive polymer.

(0116) Figure 11A shows the structure of Figure 11 following an additional processing step of depositing metal 45 onto material 39B of region “W2” and through holes 42 to establish high electrical conductivity from top surface 46 to bottom surface 47. Preferably this metal deposition is by electroplating although chemical and vapor deposition techniques could be used. Should electrodeposition be chosen to deposit metal 45, a DER would be a preferred choice for material 39B.

(0117) Figures 12-14 represent an embodiment of a structure useful for the interconnection of photovoltaic cells. A supporting substrate structure which takes the form of a substantially planar solid or foam web is generally indicated by 50. Unit of substrate 50 comprises electrically conductive resin sheet 51 and electrically insulating joining portion region 52. Region 52 has non-conductive top and bottom surfaces 53 and 54 respectively. Electrically conductive region 51 has a top, light incident side top conductive surface 55 extending between a first terminal edge 56 and a second terminal edge 57 of conductive surface 55. Width X-51 defines first and second terminal edges 56 and 57 respectively. Electrically conductive region 51 also has a bottom surface 58, length Y-51 and thickness Z-51. It is envisioned that Y-51 can be much greater than X-51 such that unit of substrate 50 could be processed in a “continuous” roll-to-roll fashion. Top surface 55 of conductive sheet 51 can be thought of as having top collector surface 59 and top contact surface 60 separated by imaginary insulating boundary 61. The substrate unit 50 may be fabricated in a number of different ways. Electrically conductive

sheet 51 can comprise an extruded film of electrically conductive polymer joined to a strip of compatible insulating polymer 52 at or near terminal edge 56 as illustrated in Figure 13. Alternatively, the conductive sheet may comprise a strip of electrically conductive polymer 51A laminated to an insulating support structure 62 as illustrated in section in Figure 14. In Figure 14, electrically insulating joining portions 52A are simply those portions of insulating support structure 62 not overlaid by sheets 51A.

(0118) Figure 13A shows joining of three substrate units 50 achieved by joining the terminal edge 57 of a first sheet 51 to the insulating joining portion 52 of another unit. Such joining can be achieved in a number of ways such as coextrusion, heat bonding, adhesive joining etc.

(0119) It is contemplated that electrically conductive sheets 51 may comprise materials in addition to the electrically conductive polymer. For example, a metal may be electrodeposited to the electrically conductive polymer for increased conductivity. In this regard, the use of a directly electroplateable resin (DER) may be particularly advantageous. DER's cover with metal rapidly by lateral growth of electrodeposit. In addition, selective metal coverage of a multi material structure is readily achieved when one of the materials is DER. For example, were region 51 shown in Figure 13A to comprise a DER, exposing the Figure 13A structure to an appropriate electroplating bath would result in rapid metal electrodeposition of region 51 only while region 52 would remain unplated. This is illustrated in Figure 13B. Figure 13B shows the cross sectional structure of the multiple units after an additional processing step of electrodepositing metal 65 onto the conductive sheets 51. Highly selective metal deposition is achieved.

For reasons previously taught in this disclosure, a sheet 51 comprising a DER is eminently suitable to achieve such selective deposition, especially on the expansive surfaces envisioned for many solar collectors. The fact that DER's are readily fabricated either as bulk compositions or coatings qualifies DER's as being eminently suitable to accomplish selective electrodeposition using web processing.

(0120) Referring now to FIG. 15, the starting material for yet another embodiment is illustrated in plan view. Web, mesh, or fabric strip 70 is characterized by having a width "W" and a length "L". It is contemplated that length "L" can be considerably greater than width "W". Thus length "L" could be generally described as "continuous" or being able to be processed in a roll-to-roll fashion.

(0121) FIG. 16, a greatly magnified plan view of a portion of the structure of FIG. 15, shows the fabric 70 comprising fibrils 71 interwoven to form a sturdy structure. Holes 72 are present among the interwoven fibrils. It is understood that the fibrils need not be actually interwoven as shown. Equivalent structures comprising fibrils and holes, such as polymeric non-woven fabric or adhesively bonded fibril mats, can be employed.

(0122) FIG.s 17 and 18 are sectional views of the embodiment of FIG. 16 taken substantially along line 17-17 and line 18-18 of FIG. 16 respectively.

(0123) Referring now to FIG. 19, there is shown the material shown in FIG. 15 following an additional processing step. The material of width "W" is now generally designated as 75 to indicate this additional process step. Width "W" has been further defined as comprising three minor widths "W1", "W2", and "W3". Each of these widths "W1", "W2", and "W3" is understood to extend along length "L" as indicated.

(0124) FIG. 20 is a greatly magnified plan view of the portion of FIG. 19 structure identified as minor width “W2”. Portions “W1” and “W3” of FIG 19 can remain unchanged from that structure shown in FIG 16. In contrast to the plan view shown in FIG. 16, the structure of FIG. 20 appears continuous in the two-dimensional plan view. This continuity results from coating the fibrils with an electrically conductive coating. The structure of the coated fibrils is best shown in the sectional view of FIG. 21, which is a view taken substantially along line 21-21 of FIG. 20. In FIG. 21, fibrils 71 in the region “W2” have been coated with electrically conductive coating 80. It is anticipated that coating 80 and the deposition process for applying coating 80 can be chosen from any number of suitable techniques. Included in such techniques are painting, dipping, or printing of conductive inks, laminating, and masked chemical or vapor deposition of metals or other conductive materials. In the case of a temperature resistant fabric such as fiberglass, deposition of a low melting point metal such as solder could be employed. A particularly advantageous coating 80 to prepare the structure of FIG. 21 is DER applied using an ink or paint solution or paste. The DER is inexpensive, and readily formulated and applied from solution form. It is clear to one of normal skill in the art that portion W2 could comprise a solid DER fabric replacing or in addition to the DER coated fabric actually shown in the embodiment. Alternatively, the W2 region could consist of a mixture of fibrils comprising DER (either coated or solid) and other fibrils, including insulating fibrils, which would remain unplated in subsequent processing steps.

(0125) The important feature of the structure of FIG. 21 is that through-hole electrical communication extends from the top surface 81 to the bottom surface 82 in the region

defined by “W2” of Figure 19. This situation is readily achieved by using the coated fabric approach of the present embodiments.

(0126) FIG. 22 is a sectional view similar to FIG. 21 following an additional optional process step. In FIG. 22, the electrical conductivity and mechanical and environmental integrity of the structure is further enhanced by applying an additional highly conductive coating 85 overlaying coating 80. This subsequent coating 85 can be conveniently applied by metal electrodeposition. In this case, 80 is preferred to be DER. The structure of FIG. 22 gives highly conductive communication, equivalent to a metal screen, from top surface 81 to bottom surface 82 in region “W2” by virtue of the through-hole electrodeposition.

(0127) Figure 23 illustrates the starting structure for another embodiment. In FIG. 23, highly electrically conducting material 92,94 is supported by substrate 96. Material 90 represents a material that can be characterized as electrically resistive in nature.

(0128) Figure 24 taken in conjunction with FIG. 25 illustrates the FIG 23 structure following an additional processing step. This additional processing step accomplishes deposition of Directly Electroplateable Resins 98,100. Materials 98,100 are deposited to slightly overlay electrically conductive material 92,94 respectively. Materials 98,100 are also deposited to slightly overlay electrically resistive material 90.

(0129) Figure 26 illustrates the FIG. 25 structure following an additional processing step of electroplating metal-based material 102,104. Materials 102,104 extend continuously from the highly electrically conductive materials 92,94 to the resistive material 90. The electrodeposits readily cover materials 92,94 due to their high conductivity.

Electrodeposits 102,104 readily cover DER materials 98,100 due to the rapid growth of

metal electrodeposit over DER materials. Metal electrodeposits 102,104 are shown to slightly overlay resistive material 90. Resistive material 90 does not completely cover with electrodedeposit due to a combination of relatively high resistance and lack of growth rate acceleration. Resistive material 90 could for example be similar to DER compositions 98,100 but absent the growth rate accelerator present in DER. Thus a continuous robust electrical connection is achieved between materials 92,94 and resistive material 90. Because of the rapid coverage with electrodeposit of materials 92,94 and DER materials 98,100 the amount of electrodedeposit overlap on resistive material 90 can be held to a minimum required to achieve electrical contact.

(0130) Figure 26A shows an embodiment following an additional optional processing step of laminating a polymeric film 103 over the surfaces of substrate 96, electrodeposits 102,104 and material 90. Film 103 may be useful for environmental protection, decoration, or the like. Such subsequent application of additional materials onto the selectively electroplated article is not considered part of the present invention. However, it is important for clarity in the specification and claims of the present invention to note that when reference is made to a surface or surface portion defined by a particular claimed element of material such as an “electrically conductive material”, that surface or surface portion may not actually be formed by or constitute that claimed element of material. Rather the claimed element or material defining a said surface or surface portion may be overlayed by a subsequently deposited material which does not constitute an essential element of the claimed invention. For example, in FIG. 26A “a surface portion defined by

resistive material" would be indicated by the dimension "R". "A surface defined by an electrodeposit" would correspondingly be indicated by "E".

(0131) Figure 27 is a sectional view of a structure similar to FIG. 26 of an alternate embodiment. In FIG. 27 a structure similar to that of FIG. 26 is designated with like numerals and the additional letter "a". In FIG. 27 it is seen that insulative material 106 covers a portion of resistive material 90a. DER material 100a covers an additional surface portion of resistive material 90a. Following electrodeposition, electrodeposited metal-based material 104a extends from material 94a across DER material 100a to the surface of resistive material 90a left uncoated by application of insulative material 106 and DER material 100a. This surface originally left exposed is indicated by the gap defined as 108.

(0132) Figure 28 is a top plan view of yet another embodiment of the present invention. In FIG. 28, numeral 118 represents a DER while numeral 116 represents a material which can be somewhat electrically conductive. Material 116 has conductivity sufficiently low such that significant electroplating current would be impeded. As previously stated, the present inventor proposes that such a condition would begin to exist at resistivities greater than about .001 ohm-cm. At higher resistivities, materials tend to fall into the classification of resistors or semiconductors. At further higher resistivities, the materials eventually fall into the classification of insulators.

(0133) Returning now to FIG. 29, a sectional view of the FIG. 28 structure taken substantially along the lines 29-29 of FIG. 28 is shown. In FIG. 29, material 116 is shown to be contiguous with DER material 118 along boundary line 124.

(0134) Referring now to Figure 30, the FIG. 29 structure is shown following an additional processing step. This additional processing step accomplishes direct electrodeposition in a rapid way over the exposed surface of DER material 118. This rapid coverage generally emanating from the contact 122 is of course characteristic of DER materials. Material 116 is shown in FIG. 30 to be substantially uncovered with electrodeposit. This is because the resistance of material 116 is sufficiently high such that it can't readily transmit electroplating current through its bulk. The resistance of course is influenced by both the intrinsic resistivity and the cross sectional area perpendicular to the current path. A bit of electrodeposit growth over the surface of material 116 generally indicated in FIG. 30 by width "J" may occur. However, this growth will be minimal during the time required to build up the required thickness of electrodeposit 120 onto the surface of DER material 118. This selective electrodeposition is a direct consequence of the presence of the coverage rate accelerator in DER material 118 and its corresponding absence in material 116. In a quintessential example of this phenomenon, materials 118 and 116 could have the exact composition other than the presence and absence of the growth rate accelerator in 118 and 116 respectively.

(0135) The slight lateral growth over material 116 shown in FIG. 30 can be avoided if required by a structural technique illustrated in Figures 31 and 32. Figure 31 shows a sectional view similar to FIG. 29 of a joining of materials 116a and DER material 118a. However, at boundary 124, a portion of material 116a has been removed to form groove 126. Figure 32 shows the FIG. 31 structure following an additional processing step. In FIG. 32, electrodeposit 120a has grown from cathodic contact 122a over the surface of

DER material 118a including that surface of 118a forming a portion of groove 126. However, lateral growth of electrodeposition is shown to have substantially stopped at the boundary 124 separating material 116a and 118a. Electrodeposition over the surface of material 116a is impeded for three reasons. First, the relatively high resistivity of material 116a resists passage of electrodeposition current as discussed above in conjunction with FIG.'s 28-30. Secondly, the electrodeposition current path from the surface of material 116a to electrodeposit 120a, generally indicated by arrow 128 is further impeded by the reduced cross section at the neck 130 of material 116a resulting from the groove 126. Thirdly, the well-known reduction in galvanic electroplating potential due to a recess further prevents electrodeposition onto the surfaces of material 116a within the groove and especially at the base of the groove i.e. the surface of neck 130. These factors all contribute to a sharp line of electrodeposit selectivity.

Example 1

(0136) The teachings of the invention were reduced to practice using an article similar to that illustrated in FIG. 3. FIG. 3 depicts a front face housing for a cellular phone, generally identified by numeral 16. Housing 16 was fabricated in the following fashion. First, a DER formulation was injection molded to form the portion of the housing indicated by the numeral 18. The DER composition comprised a polypropylene copolymer at 65 percent, conductive carbon black at 30 percent, zinc oxide at 2 percent, MBTS at 2 percent and sulfur at 1 percent. Portion 18 was then transferred to a second position in a two shot molding process and thermoplastic elastomer 17 was injected to encompass the periphery of portion 18 as illustrated in FIG. 3. The thermoplastic

elastomer used was material produced by Advanced Elastomer Systems, Akron, Ohio and marketed under the trade name Santoprene 211-55. The elastomer was unpigmented so that any possible deterioration from the subsequent plating operation described below could be readily observed. After removal from the mold, the multicomponent housing was mounted on a plating rack, with the rack tips contacting the DER portion 18 of article 16. The article was then immersed in a standard "Watts" type nickel electroplating bath under cathodic potential. The DER portion 18 quickly covered with an adherent nickel electrodeposit in about two minutes. After coverage, the housing was further electroplated with nominally 15 micrometers copper using a standard acid copper electroplating bath. This was followed by electroplating a layer of bright nickel, nominally 5 micrometer thick, from a standard Watts-based bright nickel bath. Finally, a layer of chromium, nominally 0.2 micrometer thick, was deposited from a standard hexavalent chromium bath.

(0137) The following observations were made during the course of the process:

1. The article was molded without incident using the two-shot molding process.
2. Bonding between the polypropylene based DER and the thermoplastic elastomer was good to excellent.
3. The electrodeposit fully covered the initially exposed surface of the DER. No electrodeposition occurred on the surface of the thermoplastic elastomer.
4. Bonding of the electrodeposit to the DER material was excellent.
5. No apparent change in the properties of the thermoplastic elastomer resulted from the exposure to the electroplating solutions involved. The elastomer

remained the same natural color as the unplated parts. No deterioration of the resiliency or “soft-touch” feel was detected. Adhesion between the elastomer and the DER remained good to excellent.

6. No deterioration of the interfacial areas separating electroplated DER and unplated thermoplastic elastomer was detected. Good adhesion between the polypropylene based DER and the thermoplastic elastomer prevented penetration of electroplating solutions into interfacial areas between DER and the overmolded thermoplastic elastomer.

(0138) The result was thus a unique combination of electroplated metal and a thermoplastic elastomer. A benefit was that a housing prepared in this way is intrinsically shielded for electromagnetic interference, thereby avoiding the normal operations required for such shielding.

Example 2

(0139) The following solid ingredients were weighed out:

1. 33 grams of Kraton (Kraton 1450 – Kraton Polymers)
2. 16.5 grams of carbon black (Vulcan XC-72 – Cabot Corporation)
3. .5 grams of elemental sulfur

(0140) These solid ingredients were mixed and dissolved in approximately 10 ounces of a Trichlorethylene solvent. This produced a fluid ink/coating formulation which, after drying, consisted of:

1. Kraton – 66%

2. Carbon Black – 33%

3. Sulfur – 1%

(0141) This ink/coating solution was then silk screened onto a piece of Mylar plastic film in the form of an RFID antenna pattern. The antenna pattern was allowed to dry and then was immersed as a cathode in a standard Watts nickel plating bath. The antenna pattern covered quickly with nickel electrodeposit. An approximately .0003 inch thick copper layer was subsequently electroplated on the nickel surface from a standard acid copper bath. This resulted in a highly conductive antenna pattern. The selectively electroplated structure so obtained performed well when tested as an antenna.

(0142) The following observations were made during the course of the process:

1. It was possible to silk screen the DER based coating with very good line definition and a minimum of line separation.
2. Very thin coatings of DER, even those with thicknesses less than .001 inch, were able to be rapidly electroplated.
3. There was no evidence of any significant metal coverage in areas other than those coated with DER.
4. Bonding of the electrodeposit to the DER coating was excellent.

Example 3

(0143) A DER composition comprising a high flow polypropylene copolymer (SC917 from Montell) at 65%, conductive carbon black at 30%, zinc oxide at 2%, MBTS at 2% and sulfur at 1% was compounded. This DER composition was then combined with an

unfilled polypropylene copolymer (8523 from Montell) using dual shot (or two shot) molding, whereby the DER composition formed an antenna pattern. The molded part was immersed as a cathode in a standard Watts nickel plating bath. The DER antenna pattern covered quickly with nickel electrodeposit. An approximately .0005 inch thick copper layer was subsequently electroplated on the nickel surface from a standard acid copper bath. This resulted in a highly conductive selectively electroplated antenna pattern. The structure so obtained performed well when tested as an antenna.

(0144) In the embodiments and examples, metal-based electrodeposits are shown to form surface portions of the article. It is understood that these metal-based electrodeposits could be further coated with additional electrically conducting or electrically insulating materials to achieve benefits characteristic of those materials. For example, the electrodeposit could be laminated with a polymeric layer for environmental or decorative reasons. For purposes of this invention, a surface defined by an electrodeposit or other material need not be a surface actually formed by that material, rather it is the surface shape or pattern characteristic by the referred to materials even though they may be underlying other materials.

(0145) It is important to recognize that many known or useful articles could be manufactured using the teachings described above. These include but are not limited to, many electrical circuits, electrical traces, circuit boards, antennas, capacitors, induction heaters, connectors, switches, resistors, inductors, batteries, fuel cells, coils, signal lines, power lines, radiation reflectors, coolers, diodes, transistors, piezoelectric elements, photovoltaic cells, emi shields, biosensors and sensors.

(0146) It is important to recognize that the unique design and process taught by the present disclosure is accomplished in a substantially fully additive fashion. No wasteful and costly material removal steps are needed to achieve the selective metal patterns and structures envisioned. This is a significant advantage over the prior art.

(0147) Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications, alternatives and equivalents may be included without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications, alternatives and equivalents are considered to be within the purview and scope of the invention and following claims.